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16. ABSTRACT

An integrated gas chromatography/Fourier transform infrared spectrometry (GC/FT-IR) system developed for the analysis of environmental pollutants is described. The versatility of the system allows the utilization of many different techniques of sample introduction and manipulation during analysis. The sample can be introduced by direct injection or thermal desorption from an adsorbant cartridge and can then be separated on one of two capillary columns and detected by FT-IR or an FID. Cold traps and collection cartridges incorporated in the system permit recovery and additional fractionation of samples. Recovered samples and sample fractions can then be re-analyzed by GC/FT-IR or subsequently analyzed by GC/MS or other methods.

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An Integrated GC/FT-IR System for the Analysis of Environmental Pollutants

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Key Words:

GC/FT-IR
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Summary

An integrated gas chromatography/Fourier transform infrared spectrometry (GC/FT-IR) system developed for the analysis of environmental pollutants is described. The versatility of the system allows the utilization of many different techniques of sample introduction and manipulation during analysis. The sample can be introduced by direct injection or thermal desorption from an adsorbent cartridge, and can then be separated on one of two capillary columns and detected by FT-IR or an FID. Cold traps and collection cartridges incorporated in the system permit recovery and additional fractionation of samples. Recovered sample and sample fractions can then be re-analyzed by GC/FT-IR or subsequently analyzed by GC/MS or other methods.

1 Introduction

The nondestructive mode of operation of the Fourier transform infrared (FT-IR) spectrometer used as a detector for gas chromatography (GC) has many advantages for the assessment of environmental pollutants. The GC/FT-IR system provides both chromatographic and spectral information necessary for characterization and identification of sample components. Because GC methods are widely used for the analysis of environmental pollutants [1,2], a versatile interface between the gas chromatograph and the FT-IR light pipe has been developed to enhance the potential of the GC/FT-IR system.

The interface provides for sample recovery, enrichment of the sample, and isolation of fractions of the sample. The sample can be introduced into the system by several methods, viz. direct injection, thermal desorption from adsorbent cartridges, or from cold traps. The delayed injection technique (DIT), recently reported [3], could easily be adapted and used in various ways in the GC/light pipe interface.

The sample can be rechromatographed on one of several different GC columns, although the system is presently limited to two columns. Careful selection of the columns can decrease the required analysis time and maximize the amount of unique information obtained about a given sample. The GC/light pipe interface can greatly reduce the amount of sample handling involved in the analysis of complex organic samples.

2 Experimental

2.1 Infrared Spectrometer

A Digilab FTS-14 C/X infrared spectrometer controlled by a NOVA 3/12 minicomputer was used. The spectrometer was equipped with a liquid nitrogen (LN_2) cooled mercury cadmium telluride (MCT) detector. The system optics were modified (**Figure 1**) to accommodate a gold-coated light pipe [4,5] with an internal diameter of 1 or 2 mm and a length of 25 to 80 cm.

The GC/FT-IR system (**Figure 2**) was operated using the Gas Chromatography/Infrared Fourier Transform Software (GIFTS) developed in our laboratory for the analysis of environmental samples [6]. The data collection subroutine was modified [7] to allow for a timed data acquisition rate (1 interferogram per second) and a real time display of the infrared reconstructed chromatogram (IRC) [8]. The real time display helped to facilitate the control by the user of the GC and GC/FT-IR interface and the intercomparison of chromatographic runs.

2.2 Gas Chromatograph

A Varian Model 3700 gas chromatograph with flame ionization detector (FID) was modified as described below. In addition, the chromatograph was equipped with a capillary injector-splitter system. Two capillary columns from Scientific Glass Engineering, Inc., (Austin, TX) were used. One was an SP-2250, glass, SCOT column (0.5 mm I.D., 30 m long). The second was an OV-101, flexible, vitreous silica, WCOT column (0.2 mm I.D., 50 m long).

For the organic test mixture (**Table 1**), the GC oven was programmed with a 5-minute hold at 40°C and then at 10 degrees per minute to 200°C. For the environmental sample, the oven was programmed with a hold for 4 minutes at 50°C, then at 8 degrees per minute to 250°C and with a hold at 250°C for 10 minutes.

**) Present address: Hercules Research Center, Hercules, Inc., Wilmington, DE, USA.

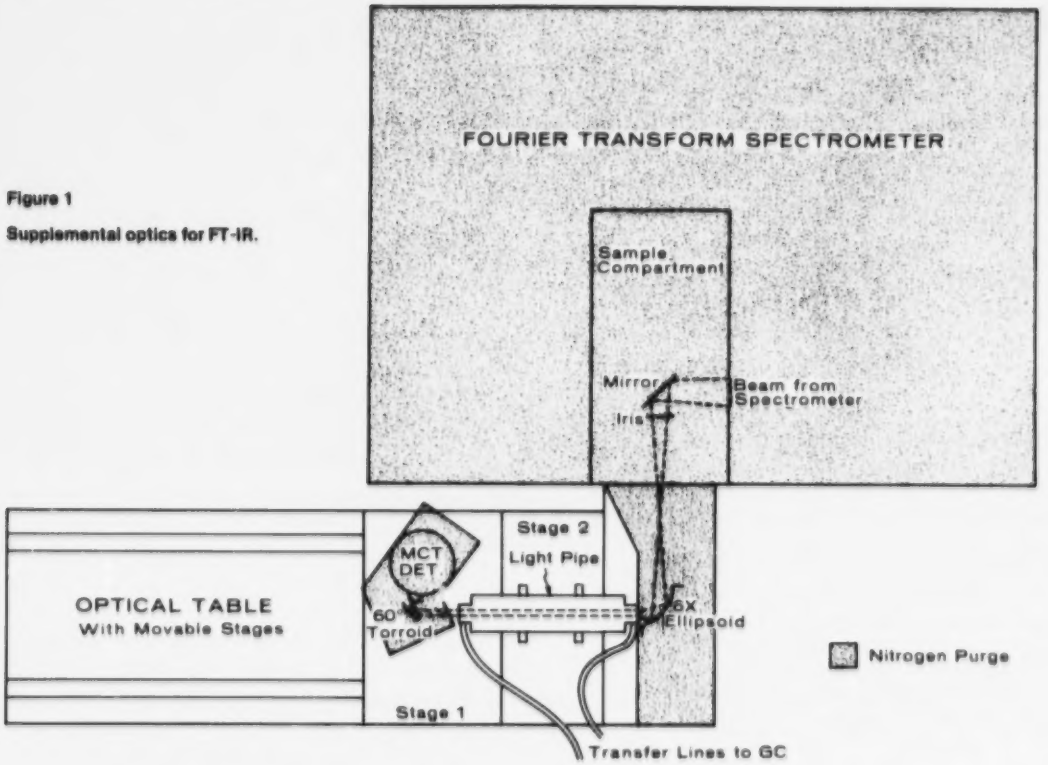


Figure 1

Supplemental optics for FT-IR.

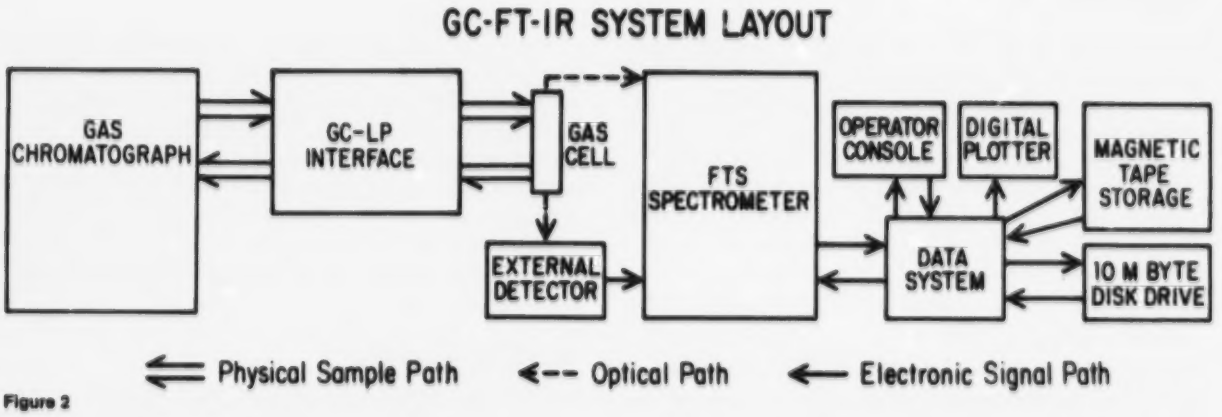


Figure 2

Block diagram of GC/FT-IR system.

2.3 GC/FT-IR Interface

The chromatograph was modified to accommodate an oven enclosure to house several Valco switching valves. The heating block from a Valco HVE-6, heated enclosure was used in the oven. The two packed column GC injector ports were removed and replaced with two copper tubes (7.6 cm long, 1.6 cm O.D.). The tubes provided a heated passage for transfer lines between the GC oven and the valve oven. The transfer lines to the light pipe passed out through the wall of the valve oven in a 1/4 in copper tube, which was wrapped with heating tape.

The GC/FT-IR interface was constructed in the valve oven using 4-port, 6-port, and 8-port valves. Stainless steel tubing (1.6 mm O.D., 0.8 mm I.D.) was used for all port-to-port connections. A short (3 cm) piece of stainless steel tubing was also used to connect each of the GC columns to their respective valve ports. This facilitates replacement of columns while the valves are at their operating temperature of 250°C.

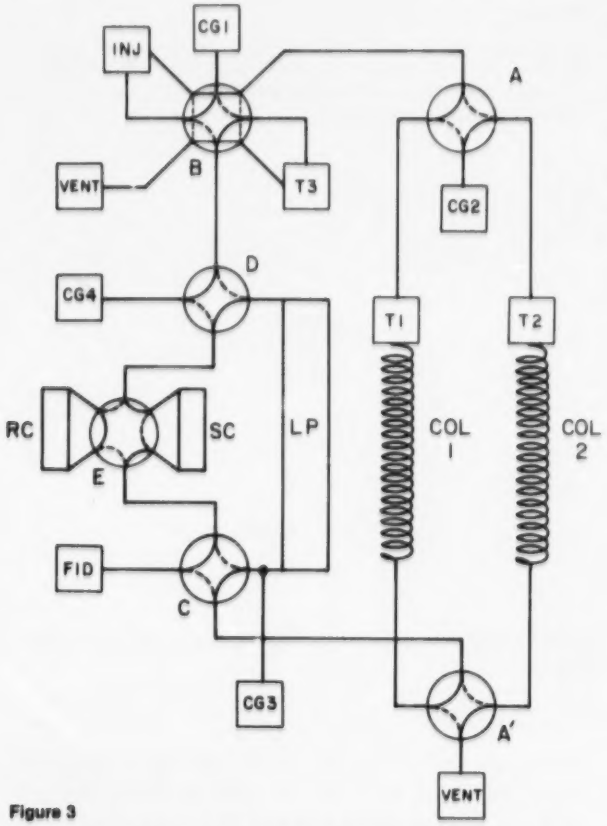


Figure 3

GC/light pipe interface. Valves: A and B have 8 ports, C and D ports, and E 6 ports. Valve a is shown as two 4-port valves (A and A') in the diagram. Helium carrier gas is supplied by the GC capillary source (CG1) and two, flow regulated sources (CG2 and CG3) plus a regulated helium tank (CG4). Other parts of the interface are: INJ capillary injector port; T3 auxiliary cold trap; T1 and T2 on column cold traps; COL1 and COL2 capillary columns; FID flame ionization detector; SC sample cartridge; RC jumper or recovery cartridge; LIGHT PIPE.

Table 1

Organic test mixture with chromatographic peak identifications.

Letter	Component
A	Methanol
B	Acetone
C	Methyl acetate and methylene chloride
D	Chloroform
E	1,4-Dioxane
F	Toluene
G	Ethylbenzene
H	Anisole
J	m-Dichlorobenzene

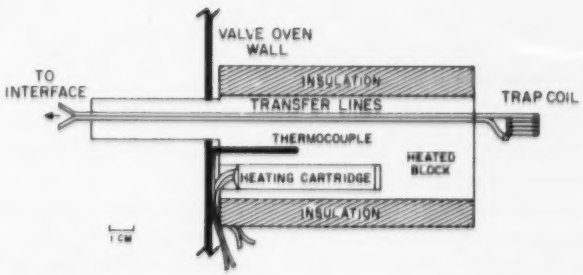


Figure 4

Cross section of auxiliary trap and housing.

The GC/FT-IR interface (**Figure 3**) was maintained under a helium purge. All the helium was passed through Varian filter cartridges of activated charcoal and 13X molecular sieve beads. The GC capillary carrier gas supply (CG1) was used for the chromatographic analysis. Another carrier gas source (CG3) provided make-up gas to the light pipe and a further one (CG2) supplied gas to purge analyte from a sample collection cartridge (SC) into the auxiliary cold trap (T3). The supplemental helium from the regulated tank was used to purge the capillary column not being used for analysis.

Each on-column trap (T_1 and T_2) was conctructed using a piece of Teflon® tubing (140 cm x 3.2 mm O.D.). A small slit was made in the tube about 40 cm from one end. The head of the column was passed into the opposite end of the tube and out the slit. The slit was wrapped with Teflon® tape to close the opening. Having inserted the column into the chromatograph, the free end of the Teflon® tube was passed out of the GC oven. Liquid nitrogen was passed through the tube to provide an on-column cold trap at the head of the capillary column.

The auxiliary trap (**Figure 4**) was constructed using a coil of 1.6 mm O.D. stainless steel tubing that passed through an insulated heating block and into the valve oven enclosure where it is attached to valve B. The trap may be heated by inserting into the trap coil a preheated 100-watt cartridge heater fitted with a collar that acts as a mechanical stop and thermocouple retainer. The trap may be cooled by liquid nitrogen sprayed from a perforated copper tube nozzle that can be inserted inside the trap coil. A slotted cylindrical cap is placed over the trap coil to confine the liquid nitrogen to its immediate vicinity when cooling the trap.

Charcoal sample cartridges were obtained from SKC, Inc., or made in the laboratory. The commercial cartridges were modified by removing the polyurethane foam plugs and all

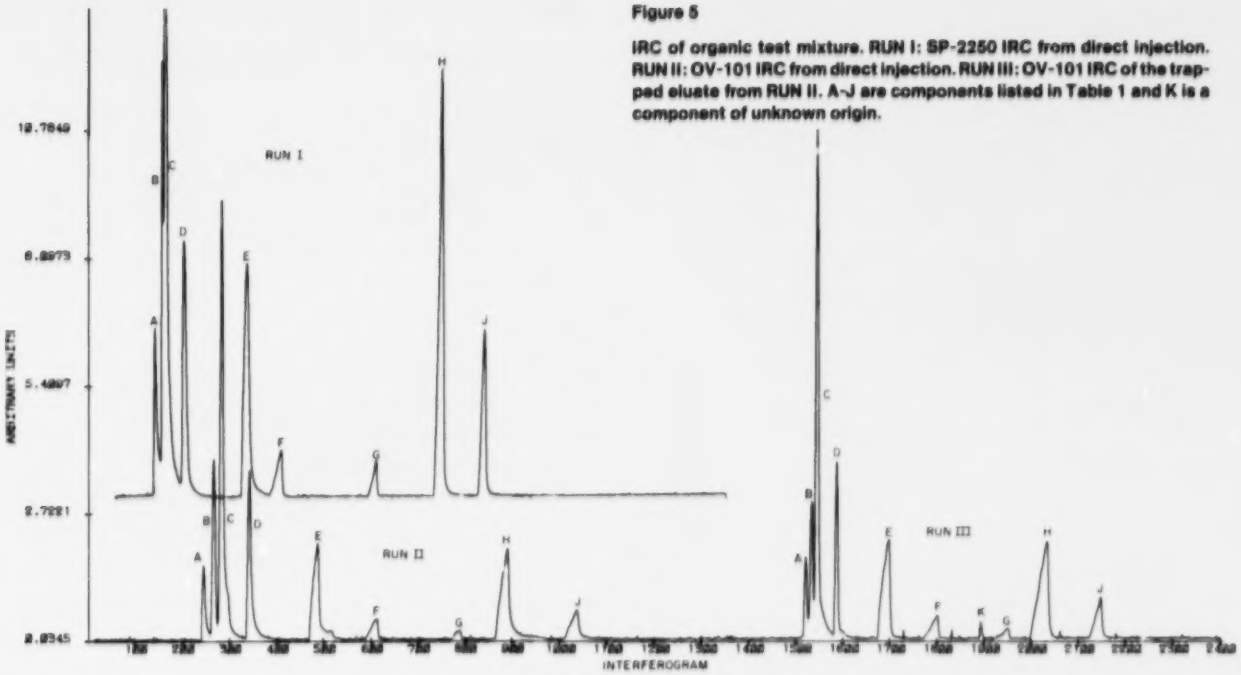


Figure 5

IRC of organic test mixture. RUN I: SP-2250 IRC from direct injection. RUN II: OV-101 IRC from direct injection. RUN III: OV-101 IRC of the trapped eluate from RUN II. A-J are components listed in Table 1 and K is a component of unknown origin.

but 30 mg of the charcoal. The excess charcoal was transferred to glass tubes (6 cm x 6 mm O.D.) to make additional cartridges. The charcoal was held in place by plugs of glass wool. For the preliminary work undertaken in this project, the sample cartridge was attached to the system using 1/4 in (6.4 mm) to 1/16 in (1.6 mm) reducing unions, Vespel ferrules, and 1/16 in (1.6 mm) stainless steel tubing. The cartridge was positioned on the top of the valve oven enclosure. The cartridge and exposed transfer lines were heated by means of heating tape. A thermocouple was used to monitor the temperature of the cartridge.

2.4 Chemicals

The organic chemicals used in the preparation of the organic test mixture were obtained from Burdick and Jackson Laboratories and Chem Service. The test mixture consisted of equal volume portions of the 10 organic compounds listed in **Table 1**. Unless otherwise indicated, splitless injection of 0.8 µl of the test solution or sample was used for each chromatographic run in this work.

3 Results and Discussion

The GC/light pipe interface has proven to be highly versatile. Several examples are given using the organic test mixture listed in Table 1.

Example 1. The mixture was chromatographed on both columns. The IRCs are shown in **Figure 5** (RUN I and RUN II).

The sample eluted from the OV-101 column was trapped in the auxiliary cold trap (T3) after passing through the light pipe. The trapped eluate was then flash vaporized using a preheated cartridge heater and chromatographed a second time on the OV-101 column (Figure 5, RUN III).

Example 2. The organic test mixture (0.2 µl) was desorbed from a charcoal cartridge into the auxiliary trap T3 and then chromatographed on the SP-2250 column after being flash vaporized from T3 (**Figure 6**). The desorbed material was passed through the light pipe and collected in T3. The IRC for this step is shown as a broad peak (M) in Figure 6. Carbon dioxide was also desorbed from the cartridge and chromatographed (Figure 6, Peak P). This chromatogram of Figure 6 agrees with Run I of Figure 5 from the direct injection of the same quantity of test mixture. In the chromatograms in Figures 5 and 6, methylene chloride and methyl acetate are seen to coelute (Peak C). The spectrum of the coeluted peak is shown in **Figure 7**. The thermal desorption step in this example may be adapted to pyrolysis or gas evolution analysis [9].

Example 3. The sample, when flash vaporized from T3, was fractionated (**Figure 8**). By positioning the auxiliary trap in place of a sample cartridge (SC), the evolution of material from the trap could be monitored during flash vaporization as the vaporized material passed through the light pipe. The spectra for each peak were run through the GIFTS library search file to identify the major component of each peak. this technique could easily be extended to the on-line analysis of components separated by distillation processes.

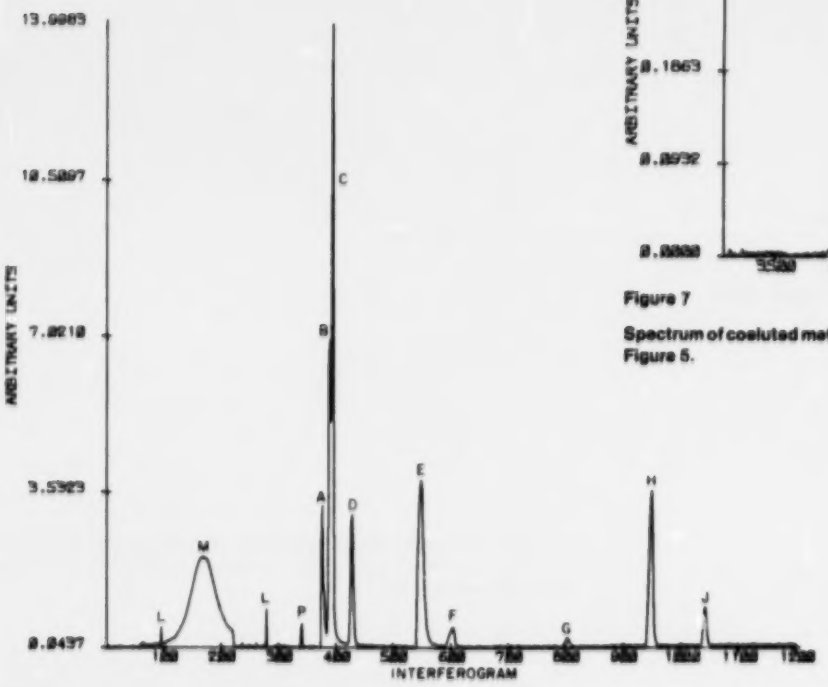


Figure 6

IRC of organic test mixture desorbed from carbon cartridge. A-J are components listed in Table 1, L are noise spikes, M is IRC of cartridge desorption, and P is carbon dioxide.

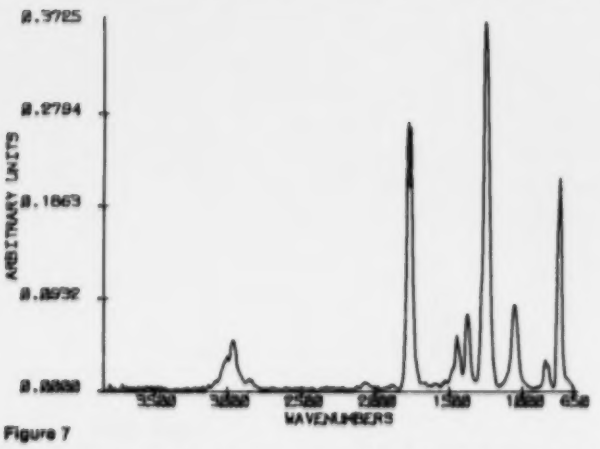


Figure 7

Spectrum of coeluted methylene chloride and methyl acetate from Run I, Figure 5.

Example 4. The on-column trap (T1 and T2) did not function as well as T3. Because the on-column trap was not heated, other than by the environment in the chromatograph oven, slug injection was not obtained. This led to ghost peaks and band broadening. In addition, a low run-to-run reproducibility was observed when using the on-column trap. **Figure 9** compares two chromatographic runs showing the FID chromatograms. One is from a direct injection of the organic test mixture, and the second results from using the on-column trap to collect the mixture prior to chromatography.

Example 5. With the GC/light pipe interface configuration shown in Figure 3, the gas supplies CG2 and CG3 are regulated by digital flow controllers. This allows easy control of gas purge rates for desorbing cartridges and adjusting the flow of make-up gas to the light pipe. Make-up gas is used to reduce the band broadening caused by the dead volume in the light pipe. The dead volume is about 0.8 ml for a 2 mm I.D. x 25 cm light pipe. The use of make-up gas improves the IRC obtained, albeit at the cost of sensitivity. For this rea-

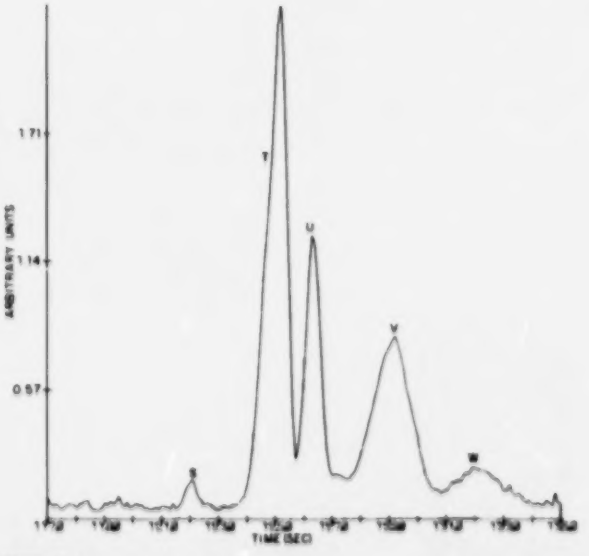


Figure 8

Sample fractionation during flash vaporization. The major components as identified by GIFTS library search are: S, not identified by the search; T methyl acetate; U 1,4-dioxane; V water; and W m-dichlorobenzene.

Figure 9

Comparison of on-column trapping (top) versus direct injection (bottom) of organic test mixture using FID. A-J are components listed in Table 1.

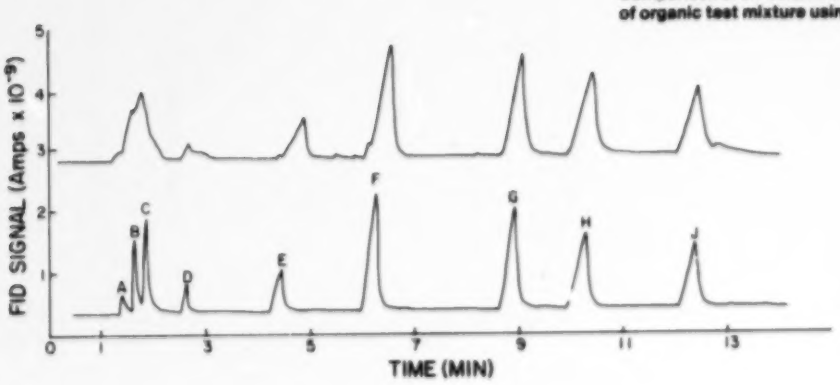


Figure 10

Effect of make-up gas on light-pipe signal. Top: 2 cm³/min column flow rate with no make-up gas. Bottom: 2 cm³/min column flow rate plus 15 cm³/min make-up gas.

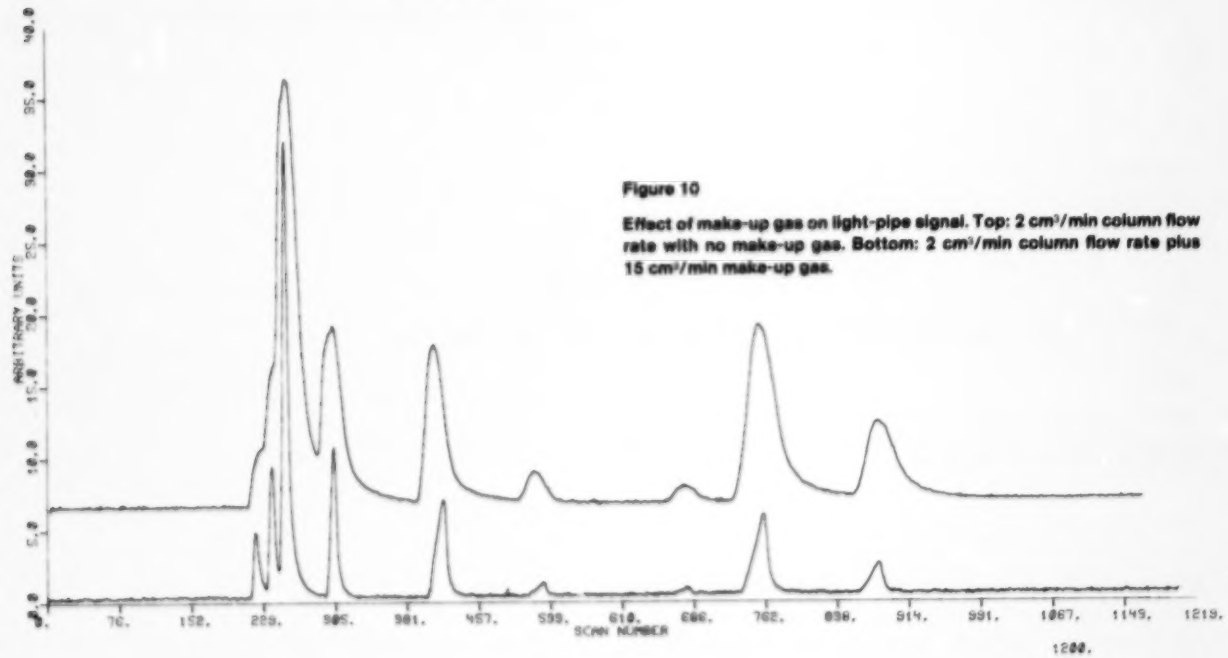
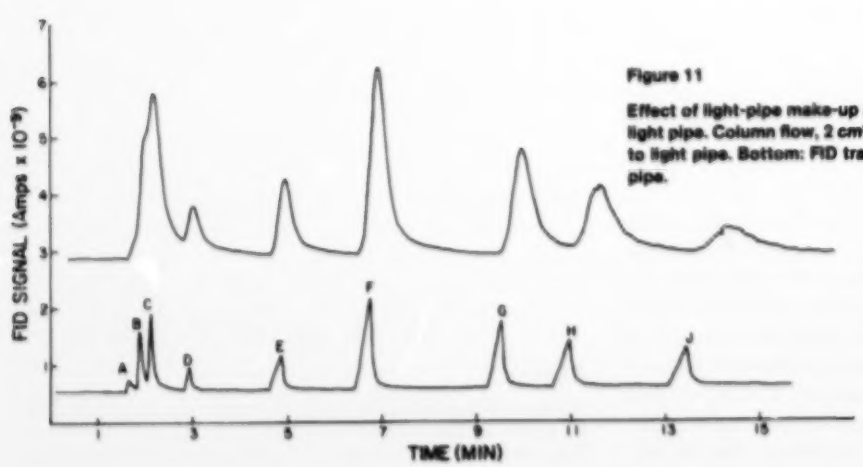


Figure 11

Effect of light-pipe make-up gas on FID chromatograms with FID after light pipe. Column flow, 2 cm³/min. Top: FID trace with no make-up gas to light pipe. Bottom: FID trace with 15 cm³/min make-up gas to light pipe.



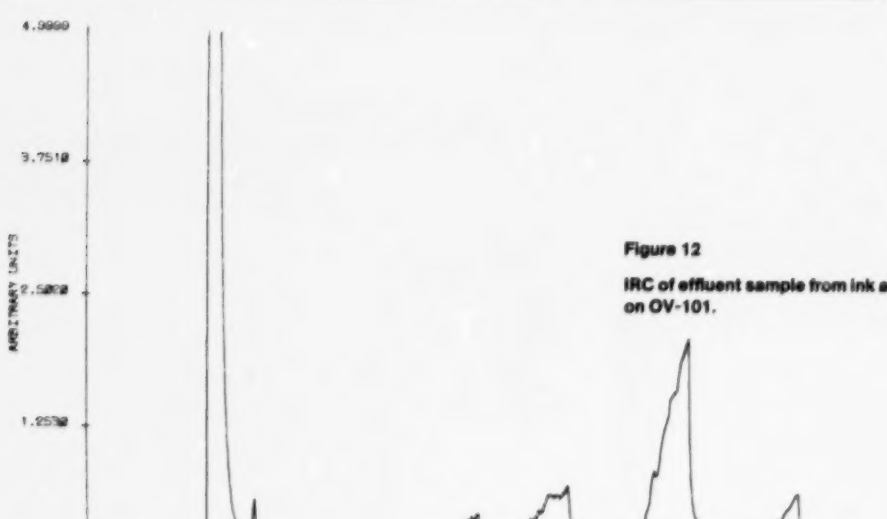


Figure 12

IRC of effluent sample from ink and printing industry, chromatographed on OV-101.

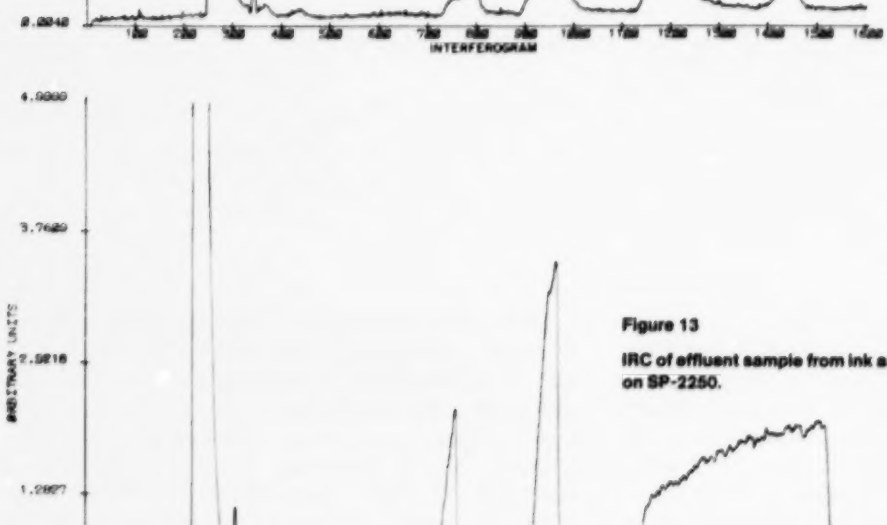


Figure 13

IRC of effluent sample from ink and printing industry, chromatographed on SP-2250.

son, the flow of make-up gas added to the column carrier gas flow should be adjusted to optimize both chromatographic resolution and sensitivity. The optimum flow is easily related to the volume of the light pipe and the peak full width at half height. **Figure 10** shows the effect of make-up gas on the observed IRC. A similar result is obtained when the light pipe and FID are operated in series and detection is by the FID only (**Figure 11**). The large dead volume of the light pipe causes a deterioration of the chromatographic peaks. The introduction of make-up gas to the light pipe helps to minimize the band broadening caused by the dead volume in the light pipe.

Example 6. An environmental sample prepared from waste water effluents of the printing and ink industry was chromatographed on both columns (**Figures 12** and **13**) with different results. In an effort to improve the spectral information of the late eluting peaks, the sample was fractionated by exploiting the capabilities of the GC/light pipe interface. The sample was chromatographed four times on the SP-2250 column with the solvent (methylene chloride) and early eluting peaks being vented off to the FID after passing through the light pipe. The fraction of the sample eluted after 850 s (interferogram No. 850, Figure 13) for all four runs was collected in T3. The enriched fraction in T3 was flash-

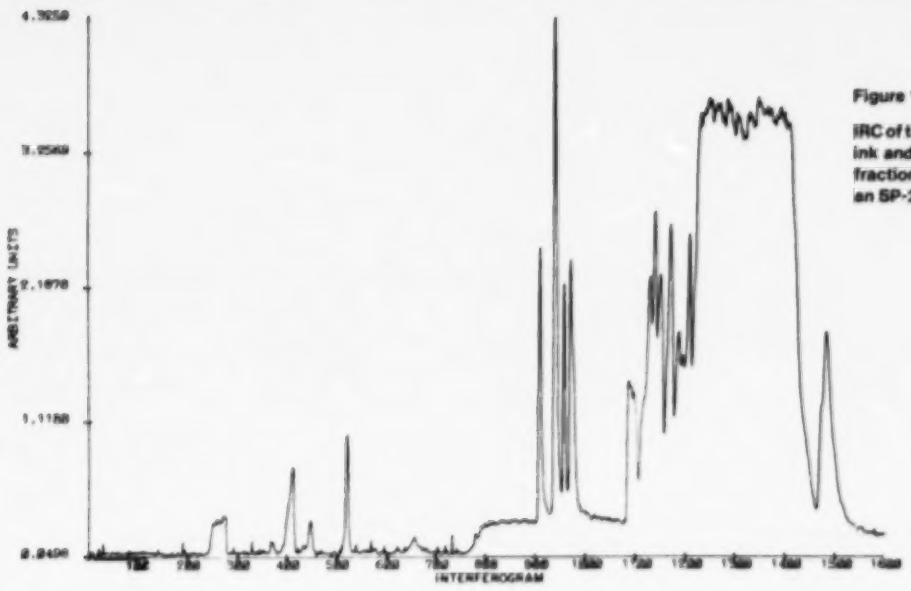


Figure 14

IRC of trapped fraction of the sample from ink and printing industry on OV-101 after fractionation and preconcentration using an SP-2250 column.

vaporized and chromatographed on the OV-101 column. The IRC of the collected fraction is shown in **Figure 14**. Comparison of the IRC in Figure 14 with those of the whole sample in Figures 12 and 13 shows several significant differences. In Figure 14, five components eluted earlier than the trapped fraction from SP-2250. The broad peak in the sample IRCs between 900 and 1000 s that is clearly seen in Figures 12 and 13 was resolved into four components. In addition, about eight partially resolved components between 1080 and 1200 s, an unresolved zone between 1220 and 1450 s, and a structured elution band that peaks at 1480 s are seen in Figure 14. The partially resolved components between 1080 and 1200 s are most probably components of the broad and most intense peak in Figure 12 that was totally unresolved from the last eluting fraction in Figure 13.

The spectra of some of the constituents of the trapped fraction together with the IRC of the fraction are shown in **Figure 15**. The first column on the left in the Figure shows the spectra of some components of the trapped fraction of the sample that elute earlier from the OV-101 column relative to elution of the trapped fraction from the SP-2250 column. Water, which appears as a flat top peak in the IRC and coincides with the solvent elution in Figures 12 and 13, is an ubiquitous artifact of the cold trapping process. It could easily come from entrained moisture or from dissolved water in the sample. The spectra of the peaks at interferogram numbers 412 and 446 are definitely those of aliphatic ketones. The spectrum of the peak at 412 matches quite well the spectrum of 5-methyl-2-hexanone, which the GIFTS search system found as the closest match. The spectrum of the peak at 446 is also that of an aliphatic ketone, probably a higher molecular weight homologue of 5-methyl-2-hexanone. The peak at 522 has a spectrum similar to that of a siloxane. The intensity ratio and frequency positions of the three absorption bands in spectrum 522 matched those of a siloxane. If the substance is a siloxane, then contamination of the sample by siloxane type compounds previously found in our laboratory air samples is a definite possibility. The other early eluting organic compounds are probably intrinsic components of the trapped fraction. It appears unlikely that they were formed during the flash vaporization of the collected fraction in view of the relatively low temperature used (200°C).

The spectra of the four components of the broad peak between 900 and 1000 s in the whole sample IRCs are shown in the second left-hand column of Figure 15. These four spectra are virtually identical except for some subtle changes in the CH stretching absorption region. These spectra matched that of carbitol, which the GIFTS search system selected from the vapor phase IR library. The four compounds are, most likely, members of the series, $C_2H_5O(CH_2CH_2O)_nCH_2CH_2OH$ of which carbitol is the first member (i.e. n = 0).

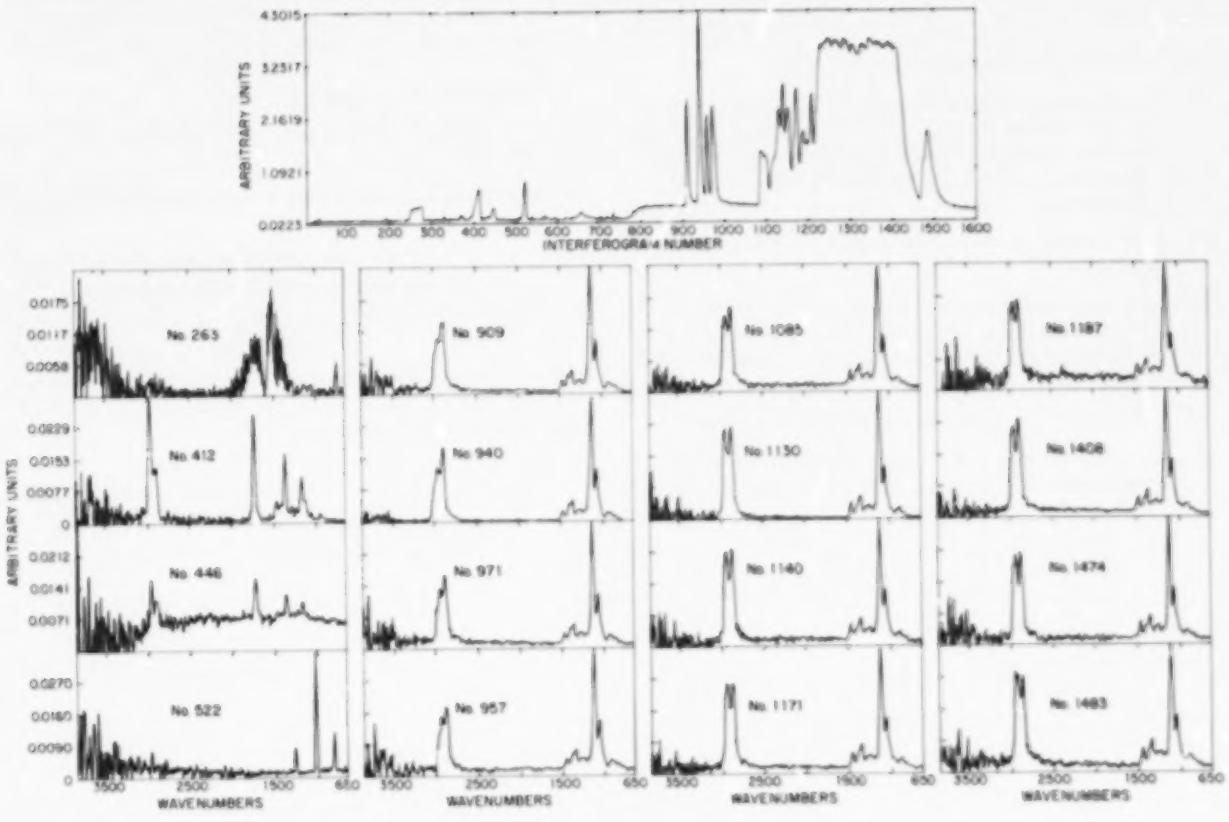


Figure 15

The IRC and spectra of constituents of the trapped fraction eluted from the OV-101.

The spectra of the partially resolved peaks appearing between 1080 and 1200 in the IRC are shown in the third column from the left of Figure 15. These spectra are typical of butoxyethoxyethanols and so are the rest of the spectra of the later eluting components of the trapped fraction that are shown in the right hand column of the Figure. It seems reasonable to conclude from this analysis that the major constituents of this industrial waste water extract are alkylethoxyethanols.

4 Conclusions

Utilizing the nondestructive nature of detection by FT-IR, the GC/light pipe interface can be used to analyze a sample prior to its recovery for further investigation. The sample can easily be re-analyzed by GC/FT-IR or subjected to analysis by GC/MS or some other means. With the GC/light pipe interface, the analysis or characterization of complex materials not necessarily requiring gas chromatographic separation becomes feasible. Where chromatographic separation is required, the device permits chromatographic resolution to be optimized by sample fractionation and on-line selection of the appropriate GC column.

The device, in conjunction with the GIFTS data collection and real time reconstruction program, should extend the use of GC/FT-IR beyond spectrochemical analysis. It could provide thermodynamic and perhaps kinetics data on experiments such as pyrolytic, thermal, oxidative, or photolytic degradation where the evolution of gaseous or volatile substances may be involved in the process.

The GC/light pipe interface could easily be computer automated, making the system readily available for routine analysis. By proper selection of chromatographic columns with similar flow characteristics, changes in the column head pressure could be eliminated in an effort to further facilitate the ease of analysis. In addition, the chromatographic integrity of the GC/light pipe interface can also be improved by the use of small internal volume switching valves [10].

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